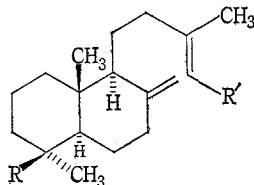
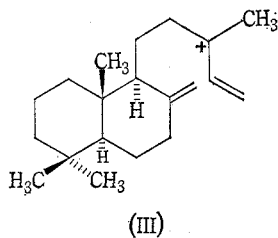
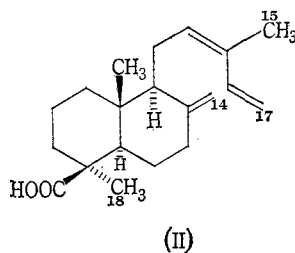
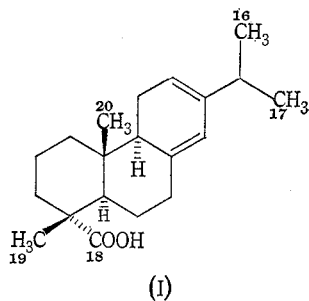


THE DITERPENE ACIDS OF *AGATHIS ROBUSTA* OLEORESIN*

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The oleoresin of the south Queensland kauri (*Agathis robusta*, dundathu pine) has been investigated by Baker and Smith^{1,2} who obtained, besides pinene, two diterpene acids, which they named dundathic (m.p. 234–235°, $[\alpha]_D +56^\circ$) and dundatholic (m.p. 101–102°, $[\alpha]_D +21^\circ$) acid.

On reinvestigation, the gum has now been found to contain the two known diterpene acids levopimaric acid (I), isolated as methyl maleopimarate, and communic acid (II), isolated as the methyl ester. The co-occurrence of these acids in the same gum is of considerable biosynthetic interest, as communic acid is bicyclic with a β (axial) C(4) carboxyl group, while levopimaric acid is tricyclic with an α (equatorial) C(4) carboxyl. The co-occurrence of bicyclic and tricyclic diterpenes, whilst known (e.g. *Dacrydium biforme*³), has not been commonly reported, and this appears to be the first occasion on which the co-occurrence of diterpene acids with both α and β C(4) carboxyl groups has been recorded. The common precursor of these acids is presumably the carbonium ion (III) which has previously been postulated⁴ to be an intermediate in diterpene biosyntheses.



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¹ Baker, R. T., and Smith, H. G., "A Research on the Pines of Australia." p. 376. (Govt. Printer: Sydney 1910.)

² Smith, H. G., *J. Soc. Chem. Ind.*, 1911, **30**, 1353.

³ Simonsen, J., and Barton, D. H. R., "The Terpenes." Vol. III, 2nd Ed., pp. 350, 477. (Cambridge University Press 1961.)

⁴ Barltrop, J. A., and Rogers, N. A. J., "Progress in Organic Chemistry." Vol. 5, p. 96. (Butterworths: London 1961.)

The resins of *A. australis*⁵ (the New Zealand kauri) and *A. alba*⁶ contain agathic acid (IV). Despite careful searching we have been unable to find evidence of agathic acid in *A. robusta*, nor have we been able to prove the presence of agathic acid (V). Thus *A. robusta* seems to be differentiated chemically from *A. australis* and *A. alba* by its lack of ability to oxygenate the bicyclic diterpene side chain.

Neither levopimaric acid (m.p. 150°, $[\alpha]_D -268^\circ$)⁷ nor communic acid (m.p. 121°, $[\alpha]_D +40^\circ$)⁸ show properties similar to those described for dundathic and dundatholic acids. Both communic and levopimaric acids are very labile compounds, and the mild isolation procedure makes them unlikely to be artefacts. The same cannot be said for dundathic and dundatholic acid since both these compounds were boiled with hydrochloric acid during the isolation procedure,² conditions under which levopimaric acid and communic acid would certainly isomerize.

Further work on the constituents of *A. robusta* oleoresin is in progress.

Experimental

The *A. robusta* oleoresin was collected as a viscous syrup from Fraser Island, Queensland. The crude resin (210 g) in ether was filtered and extracted with saturated aqueous Na_2CO_3 . The aqueous solution was acidified (dil. H_2SO_4) and the crude acids extracted into ether, washed with water, dried (Na_2SO_4), and methylated with an anhydrous ethereal solution containing an excess of diazomethane. After 12 hr at 25° the ether was washed with saturated aqueous sodium carbonate, with water, and dried (Na_2SO_4). Removal of the solvent gave the crude methyl esters (60 g).

Methyl Maleopimarate.—The crude methyl esters (2 g) were treated with an excess of maleic anhydride in dry benzene. After 24 hr at room temperature ether was added and the solution washed successively with water, 2% aqueous Na_2CO_3 , and again with water. The organic phase was dried (Na_2SO_4), and evaporated to dryness giving the adduct (0.5 g), m.p. 214–215°† (from acetone), showing no mixed m.p. depression with an authentic sample; $[\alpha]_D -38.3^\circ$ (c, 2 in chloroform) (Found: C, 72.4; H, 8.3%. Calc. for $\text{C}_{22}\text{H}_{34}\text{O}_5$: C, 72.4; H, 8.3%). The infrared curve was identical with that of authentic methyl maleopimarate with peaks (Nujol) at 1840, 1780 (anhydride); 1720 (carboxyl), 1230, 1090, 952, 930, 860, 730 cm^{-1} . The proton magnetic resonance curve was superimposable on that reported¹¹ for methyl maleopimarate with peaks at 9.38 (C(20) methyl), 8.99 (C(16) and C(17) methyls, doublet, $J = 7$ c/s), 8.82 (C(19) methyl), 6.36 (ester methyl), 4.47 (vinyl proton) τ .

Methyl Communate.—A fraction (2 g) of the oleoresin insoluble in saturated aqueous NaHCO_3 but soluble in aqueous 2% NaOH was methylated in ether with diazomethane in the normal manner to give a brown semicrystalline product (1.9 g) which was chromatographed on neutral alumina (76 g) from light petroleum. Elution with light petroleum gave methyl communate, m.p. 105–106°‡ (from methanol–ether), showing no mixed m.p. depression with authentic methyl communate; $[\alpha]_D +48^\circ$ (c, 2 in chloroform) (Found: C, 79.8; H, 10.0%. Calc. for $\text{C}_{21}\text{H}_{32}\text{O}_2$: C, 79.7; H, 10.2%). Ultraviolet λ_{max} (ethanol) 233 $\text{m}\mu$ ($\epsilon = 25,500$). The infrared spectrum was identical with that from authentic methyl communate with peaks (nujol) at 3125, 1625,

* Most workers,⁹ including ourselves, have obtained communic acid only as a labile oil.

† Literature values for methyl maleopimarate, m.p. 214–215°; $[\alpha]_D -28.9^\circ$ in chloroform.¹⁰

‡ Literature values⁹ for methyl communate, mp. 105–106°, $[\alpha]_D +48^\circ$ (c, 2 in chloroform), λ_{max} 232 $\text{m}\mu$ ($\epsilon = 25,500$).

⁵ Ruzicka, L., and Hosking, J. R., *Liebig's Ann.* 1929, **469**, 147.

⁶ Enzell, C, private communication.

⁷ Reference,³ p. 428.

⁸ Narasimhachari, N., and Rudloff, E. von, *Canad. J. Chem.*, 1961, **39**, 2572.

⁹ Arya, V. P., Erdtman, H., and Kubota, T., *Tetrahedron*, 1961, **16**, 255.

¹⁰ Graff, M. M., *J. Amer. Chem. Soc.*, 1946, **68**, 1937.

¹¹ Ayer, W. A., McDonald, C. E., and Stothers, J. B., *Canad. J. Chem.*, 1962, **41**, 1113.

995 ($-\text{CH}=\text{CH}_2$), 1790, 890 ($> \text{C}=\text{CH}_2$), 1725 ($> \text{C}=\text{O}$) cm^{-1} . The proton magnetic resonance spectrum had bands at 9.44 (C(20) methyl), 8.80 (C(18) methyl), 8.24 (C(15) methyl), 6.36 (ester methyl), 5.6–3.5 (six vinyl protons) τ .

Communol.—Methyl communate (1 g) in dry ether was reduced by lithium aluminium hydride in the normal manner to give, after chromatography over alumina, a colourless viscous oil which was twice distilled under high vacuum, $[\alpha]_{\text{D}} + 17.5^{\circ}$ * (c, 2 in chloroform) (Found: C, 83.1; H, 11.3%. Calc. for $\text{C}_{20}\text{H}_{32}\text{O}$: C, 83.3; H, 11.2%). λ_{max} . (ethanol) 233 $\text{m}\mu$ ($\epsilon = 22,000$). Infrared maxima: 3320 ($-\text{OH}$), 3070, 1640, 990 ($-\text{CH}=\text{CH}_2$), 1790, 890 ($> \text{C}=\text{CH}_2$), 1605 (conj. $\text{C}=\text{C}$) cm^{-1} . The proton magnetic resonance spectrum had peaks at 9.30 (C(20) methyl), 9.02 (C(18) methyl), 8.24 (C(15) methyl), 6.1–6.9 (complex¹² due to the C(19) protons), 3.5–5.7 (six vinyl protons) τ . The proton magnetic resonance spectrum and the purity of this communol are discussed in another communication.¹²

Agathic Acid.—The crude resin acids, when chromatographed on a charcoal-kieselguhr column under the conditions used to separate agathic acid in other experiments,¹³ gave no crystalline agathic acid and no oil with an infrared spectrum characteristic of agathic acid. Reduction of the crude Na_2CO_3 -soluble acids with lithium aluminium hydride followed by chromatography in the manner described^{13,14} for the preparation of agathadiol (VI), failed to result in the formation of agathadiol in this case.

We are indebted to Professor W. L. Meyer and to Professor H. Erdtman for samples of authentic maleopimaric acid and methyl communate; to the Department of Forestry, Queensland, and the Forest Officer, Fraser Island, for supplies of *A. robusta* oleoresin; and to Mr. G. Gilman for technical assistance.

* Literature values⁹ for communol, $[\alpha]_{\text{D}} + 18^{\circ}$, λ_{max} . 233 $\text{m}\mu$ ($\epsilon = 22,460$).

¹² Carman, R. M., and Dennis, N., *Aust. J. Chem.*, 1964, **17**, 395.

¹³ Carman, R. M., *Aust. J. Chem.*, 1964, **17**, 393.

¹⁴ Enzell, C., *Acta Chem. Scand.*, 1961, **15**, 1303.